

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 965 615 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.12.1999 Bulletin 1999/51

(51) Int. Cl.⁶: C08L 67/04, C08L 3/02,
C08J 5/18
// (C08L67/04, 3:02)

(21) Application number: 99201955.4

(22) Date of filing: 17.06.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 17.06.1998 IT TO980524

(71) Applicant: NOVAMONT S.p.A.
28100 Novara (IT)

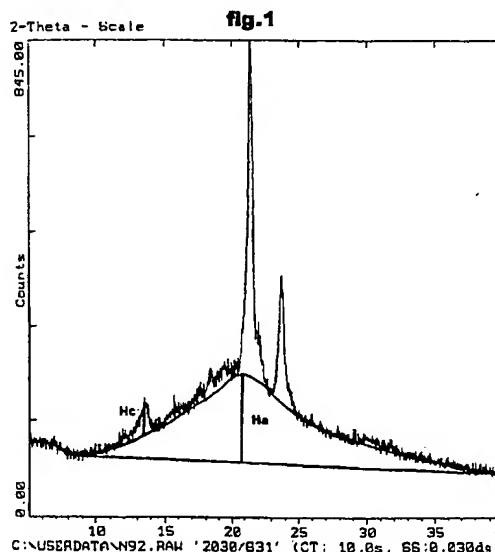
(72) Inventors:
• Bastioli, Calia
28100 Novara (IT)

• Bellotti, Vittorio
28010 Fontaneto d'Agogna (Novara) (IT)
• Del Tredici, Gianfranco
21018 Sesto Calendf. (Varese) (IT)
• Guanella, Italo
28068 Romentino (Novara) (IT)
• Lombi, Roberto
28100 Novara (IT)

(74) Representative:
Rambelli, Paolo et al
c/o JACOBACCI & PERANI S.p.A.
Corso Regio Parco, 27
10152 Torino (IT)

(54) Complexed starch-containing compositions having high mechanical properties

(57) Heterophasic compositions comprising starch and a thermoplastic polymer that is incompatible with the starch, in which the starch constitutes the discontinuous phase and the thermoplastic polymer the continuous matrix, having an impact strength greater than 30 KJ/m² (measured on blown film of 30 microns thick at 10°C and RH less than 5%), and further characterised by the presence in the X-ray diffraction spectrum of a peak at an angle 2-theta from 13 to 14° the ratio of the intensity of which to that of the peak of the amorphous starch which occurs at 20.5°, is less than 2 and greater than 0.02.



EP 0 965 615 A1

Description

[0001] The present invention relates to heterophasic polymeric compositions having a high resistance to ageing, even under conditions of low temperature and humidity, comprising thermoplastic starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase and the polymer the continuous phase.

[0002] The invention relates particularly to manufactured products which maintain high impact strength and tear strength in low humidity conditions.

[0003] It is known that products (in particular films) manufactured from compositions containing thermoplastic starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase, show a significant deterioration in their mechanical properties, in particular, their impact strength and tear strength, due to the fact that the starch gives up or absorbs water until it reaches equilibrium with the ambient humidity at its interface.

[0004] In relatively low humidity conditions, the material tends to become brittle, as the dispersed phase becomes insufficiently plasticised due to the loss of water which takes the glass transition temperature above ambient temperature.

[0005] This phenomenon can damage the interface with the matrix when the interface is not sufficiently bonded.

[0006] Under these conditions, when the starch particles constituting the dispersed phase are subjected to stress, they are unable to deform and absorb the stress, but instead remain rigid, thus initiating a tear.

[0007] Italian patent application No. T096A000890 filed by the Applicant describes compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with the starch, having improved characteristics of resistance to ageing under conditions of relatively low humidity, obtained by introducing an agent having an interfacing action during the mixing of the components. This compatibility-inducing action improves the adhesion between the matrix and the dispersed particles.

[0008] Reducing the interface tension also enables the dimensions of the particles to be reduced to submicronic values, whereby the materials have the characteristics of a polymeric alloy.

[0009] Compositions comprising starch, a thermoplastic polymer and a plasticiser are widely described in patent literature.

[0010] However, the concentrations of these plasticisers at which the mechanical properties of the compositions are greatest are never taught, nor suggested, in the prior art.

[0011] EP-A-0 327 505 describes compositions in which the plasticiser is used in a quantity of from 0.5 to 15%, preferably between 0.5 and 5% by weight, together with such quantities of water that the sum of the plasticiser and the water does not exceed 25% by weight of the compositions (the quantitative minimum of water in these compositions is 10% by weight).

[0012] W092/19680 describes compositions comprising starch, a polyester of a hydroxyacid or the corresponding lactone such as, for example, polycaprolactone, and a plasticiser usable in a quantity of from 1 to 50% by weight, preferably 1-40%, and more preferably 5-25% by weight of the composition.

[0013] The compositions preferably have a final water content of between 1.5 and 5% by weight (measured on leaving the extrusion press, before conditioning).

[0014] In the aforementioned document, there is no use of nor any indication of the existence of a possible critical range of the concentration of the plasticiser corresponding to that for obtaining very high mechanical properties, nor is there any indication of which plasticisers are suitable for this purpose.

[0015] The quantity of plasticiser used in the examples is always greater than 10% by weight of the composition.

[0016] US-5 334 634 describes compositions comprising starch, an ethylene-vinyl alcohol copolymer and a plasticiser usable in a quantity of from 0.5 to 100% by weight of the starch.

[0017] In this case also, the quantity of plasticiser effectively used is always greater than 10% by weight of the composition.

[0018] It is known that starch, in particular, its amylose fraction, forms "V"-type complexes with synthetic polymers such as polyethylene vinyl alcohol or polyethylene-acid acrylate (C.Bastioli and others in "Biodegradable Plastics and Polymers", pages 200-213; 1994, Elsevier Science). In such multiphase systems in which the synthetic polymer comprises the continuous phase and the starch the dispersed phase, the complex acts as a compatibility-inducer or phasing agent.

[0019] Similar complexes can form between starch and aliphatic polyesters or aliphatic/aromatic copolyesters. However, if, in the preparation of the compositions comprising starch and the aforementioned polyesters, relatively high quantities of the starch plasticisers are used to ensure the plasticity of the material under the conditions of use of the manufactured product and low specific energy for destructure and complexation is used, the quality of the interface is insufficient to ensure the toughness of the material at low temperatures and humidity in the presence of the plasticiser itself.

[0020] Furthermore, if plasticisers which are solid at room temperature are used in relatively high concentrations, at which the complex between starch and incompatible polymer can form in a quantity sufficient to ensure an effective

compatibility-inducing action, these plasticisers cause, in conditions changing from high to low relative humidity, brittleness in the material.

[0021] It has unexpectedly been found that it is possible to prepare heterophasic compositions comprising starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase and the thermoplastic polymer the continuous matrix, which compositions have characteristics of high impact strength even when passing from conditions of high to low relative humidity if they are prepared using a quantity of plasticiser that is liquid at room temperature comprised within a critical range wherein the concentration of the complex between starch and the incompatible polymer reaches a maximum, and a specific energy of destructure of starch higher than a certain value.

[0022] The critical quantity of plasticiser, which is preferably glycerin, is generally from 2 to 8% and preferably from 3 to 7% by weight of the starch and the thermoplastic polymer. Quantities outside this range are, however, possible, depending on the type of plasticiser and its efficacy.

[0023] The specific energy for the destructure of the starch and its complexation are comprised from 0,1 to 0,5 Kw.h/Kg, preferably from 0,15 to 0,4 Kw.h/Kg and most preferably from 0,2 to 0,35 Kw.h/Kg.

[0024] For specific energy for the destructure and complexation of the starch it is meant the energy supplied by an extruder the screw or screws of which are capable of developing a specific energy of at least 0,1 Kw.h/Kg at the extrusion temperature of 120 - 210 °C.

[0025] The specific energy is determined according to the formula: $A \times B \times C / D \times E \times F$ wherein

A = engine power

B = RPM

C = energy absorption

D = RPM max

E = energy absorption max

F = flow rate

[0026] Until now, critical values as indicated above had never been used nor suggested in prior art compositions.

[0027] It has been discovered, and this constitutes a characterising aspect of the invention, that the complex of starch and incompatible polymer reaches maximum concentration values within the aforesaid critical range.

[0028] The presence of the complexes of starch and incompatible polymer can be demonstrated by the presence in the second derivative FTIR spectra of a band at a wavelength of 947 cm⁻¹ (specific to the complex) and in the X-ray diffraction spectra of a peak in the range of 13-14° on the 2 theta scale (with Cu K_{alpha} radiation of 1.5418 Å). In both cases, the position of the band or the peak of the complex remains unchanged, even on changing the nature of the complexed polymer. Figures 1 and 2 show the X-ray and second derivative FTIR spectra, and are typical of the formulations based on starch and aliphatic polyesters (PCL in particular).

[0029] It has been found that in the X-ray spectra of the compositions of the invention, the Hc/Ha ratio between the height of the peak (Hc) in the range of 13 - 14° of the complex and the height of the peak (Ha) of the amorphous starch which appears at about 20.5° (the profile of the peak in the amorphous phase having been reconstructed) is less than 2 and greater than 0.02. In the spectrum of Figure 1, the heights Hc and Ha, are indicated for the peaks of the complex and the amorphous starch respectively.

[0030] In case of crystalline polymers with a crystallinity content higher than 30% the lower limit of the ratio Hc/Ha is 0.2; in case of amorphous polymers or polymers with a crystallinity content less than 30% the lower limit of the ratio Hc/Ha is lower than 0.2.

[0031] The heterophasic compositions of the invention therefore comprise starch, a thermoplastic polymer incompatible with the starch, a starch plasticiser or a mixture of starch plasticisers, in which the starch constitutes the discontinuous phase and the thermoplastic polymer the continuous phase, and are characterised in that they form films having characteristics of high impact strength higher than 30 Kj/m², preferably higher than 45 Kj/m² and most preferably higher than 60 Kj/m² (measured on blown film 30 micron thick at 10°C and less than 5% relative humidity) and have an X-ray spectrum having a peak at angle 2 theta in the range from 13 to 14° with an intensity related to that of the peak of the amorphous starch which appears at an angle 2 theta of 20.5° less than 2 and greater than 0.02.

[0032] The compositions are obtainable by extrusion of a melt comprising starch, the thermoplastic polymer, the plasticiser in a quantity within the critical range, and water in a quantity less than 5% by weight (measured on leaving the extrusion press, before conditioning) and supplying a specific energy of at least 0,1 Kw.h/Kg and lower than 0,5 Kw.h/Kg.

[0033] The preparation of the compositions by extrusion is carried out according to known temperature conditions, operating, for example, at temperatures of between 120 and 210°C, preferably from 130 to 190 °C.. Suitable usable extruders are those provided with screws having a "reverse" profile for more than 30% of the length of the screw (a reverse profile causes the material to advance with a piston effect).

[0034] The water content in the extrusion stage can be high in the phase of destructurization of starch and can be regulated at the end of the extrusion at the desired values of less than 5% by weight by degassing or by using a starting starch with a low water content (the water content is measured at the exit of the extruder, prior conditioning).

5 [0035] If the compositions or the manufactured products obtainable therefrom are washed with water, the plasticiser contained therein is extracted but the compositions and the manufactured product maintain mechanical properties, in particular impact strength, comparable to the properties of the film before washing. These compositions and manufactured products also form part of the invention.

10 [0036] The starch-incompatible thermoplastic polymers are preferably chosen from the aliphatic (co)polyesters obtained from hydroxyacids having 2 or more carbon atoms, and from the corresponding lactones or lactides, or from aliphatic bicarboxylic acids having 2-22 carbon atoms, and from diols having 2-22 carbon atoms, polyester-amides, polyester-urea and aliphatic-aromatic copolyesters and mixtures thereof.

[0037] These thermoplastic polymers, or mixtures thereof, have a melting point lower than 130°C and preferably lower than 110°C.

[0038] Representative examples of the polymers mentioned above are:

15 - poly-epsylon-caprolactone, polyethylene- and polybutylene-succinate, polyhydroxybutyrate-hydroxyvalerate, polylactic acid, polyalkyleneadipate, polyalkyleneadipate-succinate, polyalkyleneadipate-caprolactame, polyalkyleneadipate-epsylon-caprolactone, polyadipate of diphenol diglycidylether, polyepsylon-caprolactone/epsylon-caprolactame, polybutylene adipate-co-terephthalate, polyalkylenesebacate, polyalkylene-azelate and copolymers thereof or mixtures thereof.

20 [0039] These polymers can also be "chain-extended" with diisocyanates, polyepoxides and similar multifunctional compositions.

[0040] Poly-epsylon-caprolactone and the aliphatic-aromatic copolyesters are preferred. Other polymers which can be used are the esters and ethers of cellulose and of starch.

25 [0041] The starch-incompatible polymer is present in a quantity sufficient to form the continuous phase of the heterophasic composition. In general, this quantity is between approximately 30 and 90% by weight of the starch.

[0042] The polymers can be used in mixtures having smaller proportions of polymers of the ethylene/vinyl alcohol, ethylene/acrylic acid type and polyvinylalcohol.

30 [0043] The usable starch is native starch such as, for example, corn, potato, rice, tapioca starch, or is a physically or chemically modified starch such as, for example, ethoxylated starch, starch acetate and hydroxypropylated starch, cross-linked starch or oxidated starch, dextrinized starch, dextrins and mixtures thereof.

[0044] The starch plasticisers which can be used are polyhydric alcohols having from 2 to 22 carbon atoms, in particular, polyhydric alcohols having from 1 to 20 hydroxylated units containing from 2 to 6 carbon atoms, the ethers, thioethers and the organic and inorganic esters of these polyhydric alcohols.

35 [0045] Examples of plasticisers that can be used are: glycerine, ethoxylated polyglycerol, ethylene glycol, polyethylene glycol, 1,2-propandiol, 1,3-propandiol, 1,4-butandiol, neopentylglycol, sorbitol monoacetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate and mixtures thereof.

[0046] The compositions can also include interfacial agents of the kind described in Italian patent application T096A000890, chosen from:

- 40 a) esters of polyhydric alcohols with mono- or polycarboxylic acid having a dissociation constant pK less than 4.5 (with reference to the pK of the first carboxylic group in the case of the polycarboxylic acids), and a hydrophilic/lipophilic index (HLB) greater than 8;
 b) esters of polyhydric alcohols with mono- or polycarboxylic acid having fewer than 12 carbon atoms, pK values greater than 4.5, and HLB indexes of from 5.5 to 8;
 45 c) esters of polyhydric alcohols with C12-C22 fatty acids, having an HLB index of less than 5.5;
 d) non-ionic, water soluble surfactants, and
 e) products of the reaction between aliphatic or aromatic diisocyanates and polymers containing terminal groups that react with the diisocyanates.

50 [0047] The compositions of the invention can also contain additives such as urea in a quantity of up to 20% by weight, compounds of boron, particularly boric acid, proteins such as casein, gluten and abietinic acid or rosinic acid, natural rubbers, flame retardant agents, antioxidants, fungicides, herbicides, fertilisers, opacifiers, compositions having a repellent effect on rodents, waxes, antislipping agents (such as erucamide, calcium stearate, zinc stearate).

55 [0048] They can also contain organic and inorganic fillers from 0.5 to 70% by weight and natural fibers. The compositions of the invention find particular application in the preparation of films, sheets, in thermoforming and, in general, in all applications in which good mechanical properties of the manufactured product are required, together with high resistance to ageing, even under conditions of low temperature and humidity.

[0049] Examples of products which can be manufactured using the compositions of the invention include, in addition

to those mentioned above, bags, laminates, moulded and blown articles, expanded sheets, expanded materials, biofillers for tyres, backsheets for diapers, wrapping films, mulching films, multilayer films, sacks for mowing grass, shoppers, nonwoven fabric, toys, pet toys, dog collars, products with controlled release for use in the agricultural field, threads.

[0050] The following examples are given to illustrate and not to limit the scope of the invention.

Example 1

[0051] A mixture formed from (parts by weight):

- Globe 03401-Cerestar natural starch*	27
- Tone-787 PCL	65
- glycerine	4.5
- water	3.5
	<u>100.0</u>

* water content 12% wt

was supplied to a two screw OMC extruder of 60mm diameter, L/D = 36, RPM = 180.

[0052] The temperature profile was as follows: 60/145/175/180x4/155x2°C.

[0053] It was operated with free degassing.

[0054] The specific energy supplied was 0,4 Kw.h/Kg.

[0055] The extruded material was pelletised. The water content was 1.3% by weight.

[0056] The pellets were used to manufacture films using Ghioldi apparatus provided with Maillefer-type screws of 60mm diameter and L/D = 30. The thermal profile was as follows: 90/120/140/150x3/147x2°C.

[0057] The film head had a diameter of 180mm.

[0058] The film produced, approximately 30 μ thick, was tested as such for its mechanical properties. A sample of the same film was on the other hand immersed in water for 24 hours to remove the starch plasticisers; after this, the samples taken from the washed film were left to condition for 72 hours in an environment with a temperature and humidity equal to those used for detecting the mechanical properties.

Example 2

[0059] A mixture of (parts by weight):

- Globe 03401 corn starch	33.4
- Tone-787 PCL	54.3
- glycerine	5.8
- water	6.5
	<u>100.0</u>

was supplied to a two screw APV-2030 extruder; L/D = 35 + 5XLT; RPM = 170; thermal profile: 60/100/170x14°C.

[0060] The extruder was operated with free degassing.

[0061] The specific energy supplied was 0,17 Kw.h/Kg.

[0062] The extruded material was pelletised. The water content was 1.5% in weight.

[0063] The pellets were used to produce a sheet via cast-extrusion, using a modified AEMME extruder provided with 1:3 constant taper screws; diameter 30mm; L/D = 25; RPM = 35. The extruder had a flat head 150mm wide with a lip aperture of 0.8mm. The sheet obtained was 0.6mm thick.

[0064] A quantity of pellets was separately made into a film as described in example 1 to obtain samples to test for their mechanical properties (samples of the film as produced and washed in water).

Example 3

[0065] The test of example 2 was repeated using a composition (parts by weight) of 33.4 parts starch of the type used in example 2, 54.3 parts of Tone-787 PCL, 4.8 parts of glycerine and 7.5 parts of water. The film thus obtained was tested for its mechanical properties (film as produced and washed in water).

Comparison Example 1

[0066] A mixture formed from (parts by weight):

- Globe 03401 corn starch	33.4
- Tome-787 PCL	54.3
- glycerine	9.7
- water	5.5
	<u>100.0</u>

was mixed in an extruder and made into a film as in example 1.

[0067] The specific energy supplied was 0,22 Kw.h/Kg.

[0068] The film obtained was tested for its mechanical properties (film as produced and washed in water as in example 1).

Comparison Example 2

[0069] A composition comprising 65 parts potato starch at 6% humidity and 35 parts of a mixture of glycerine: sorbitol 1:1 by weight (sorbitol is solid at ambient temperature) was supplied to the two screw APV-2030 extruder, as used in example 1, operating with the following thermal profile: 60/100/190x14°C. Compounding was done with active degassing to obtain an extrudate having a water content of less than 0.5%.

[0070] Then, 35 parts of dried pellets and 65 parts of Tone-787 PCL were mixed in an APV-2030 extruder; the extruded material was made into pellets and finally made into a film of approximately 30 μ thickness, exactly as in example 1.

Example 4

[0071] The test of example 3 was repeated with the only difference being that 3.8 parts glycerine and 8.5 parts water were used.

[0072] The film thus obtained was tested for its mechanical properties (film as produced and washed in water as in example 1).

Example 5

[0073] A mixture formed from (parts by weight):

- Globe 03401-Cerestar natural starch	26.4
- Ecoflex®	63.8
- glycerine	5.5
- water	4.3
- Erucamide	<u>0.3</u>
	100.0

was supplied to a two screw OMC extruder of 60mm diameter, L/D = 36, RPM = 180.

[0074] Ecoflex is a registered trade mark of BASF and refers to a polybutylene adipate-co-terephthalate copolymer.

[0075] The temperature profile was as follows: 60/140/175/180x4°C.

[0076] It was operated with free degassing.

5 [0077] The specific energy supplied was 0,36 Kw.h/Kg.

[0078] The extruded material was pelletised. The water content was 1.7% by weight.

[0079] The pellets were used to manufacture films using Ghioldi apparatus provided with Maillefer-type screws of 60mm diameter and L/D = 30. The thermal profile was as follows: 120/135/145x5/140°C.

[0080] The film head had a diameter of 100mm.

10 [0081] The film produced, approximately 30 μ thick, was tested as such for its mechanical properties. A sample of the same film was on the other hand immersed in water for 24 hours to remove the starch plasticisers; after this, the samples taken from the washed film were left to condition for 72 hours in an environment with a temperature and humidity equal to those used for detecting the mechanical properties.

15

TABLE 1

PROPERTIES OF BLOWN FILM AT 23°C & 50% RH (ASTM Standard d 882)					
	Breaking Load	Breaking elongation	Modulus of elasticity	Breaking energy	Hc/Ha
20 Examples	Mpa	%	Mpa	KJ/m2	
1 as produced	37.1	880	503	8600	0.44
1 washed	31.6	747	501	7750	
25 1 cf. as produced	28.3	810	310	5640	0.07
1 cf. Washed	20.0	120	603	327	
2 as produced	31.2	880	520	8230	0.33
2 washed	25.8	637	631	6630	
30 3 as produced	29.2	756	541	6194	0.29
3 washed	21.1	539	598	4930	
4 as produced	24.5	662	632	5980	0.27
35 4 washed	20.2	521	606	4760	
5 as produced	23.1	489	136	4155	0.07

[0082] Table 2 shows the characteristics of roughness of the sheets of examples 2-4, and comparison examples 1-2.
40 A high level of roughness, although spoiling the aesthetic appearance, is critical for the printability of the sheet with printing inks.

TABLE 2

45

SURFACE ROUGHNESS	
EXAMPLE	ROUGHNESS (micron)
2	0.20
3	0.20
4	0.24
cf. 1	0.14
cf. 2	1.17

50

55

[0083] Tables 3 and 4 show test data for tear and impact traction.

TABLE 3

TEAR TESTS AT 23°C & 50% RH(*)		
Examples	Start tearing N/mm	Propagation N/mm
1 as produced	116.5	116.5
2 as produced	85.6	85.7
1 cf. as produced	64	63.8

(*) ASTM standard d-1938

TABLE 4

IMPACT-TRACTION TESTS AT 10°C AND RH < 5% (**) ON FILM OF 30 micron		
Example	Energy KJ/m ²	Load Mpa
1	110	30
2	73	24
1 cf.	6	12
2 cf.	22	23
5	145	18

(**)

The tests were carried out using instrumentation comprising a conventional "piezoelectric load cell" for detecting the energy, which cell is located on a terminal on which the end of a test specimen is fixed, 30-40 micron thick, 30mm wide and 35mm long.

[0084] A double incision was made symmetrically half way along the sample such that each incision extended over a quarter of the width of the sample. A rod was connected to the other end of the sample, which rod acts as a guide for an axially-pierced cylinder, 500g in weight. The rod terminates in a plate onto which the weight is released from a height of 5cm at a velocity of 1m/sec.

[0085] The apparatus was arranged within a climatic cell operating at 10°C and RH < 5%.

[0086] The samples were conditioned at the same temperature for 48 hours before the test.

TABLE 5

PROPERTIES OF SHEET FORMED VIA CAST-EXTRUSION			
Examples	Load Mpa	Elongation %	Modulus Mpa
2 as produced	37.3	892	271
2 washed	30.1	630	464
3 as produced	35.0	846	379
3 washed	26.2	595	550
4 as produced	32.5	745	351
4 washed	21.0	531	495

[0087] Figures 1 and 2 show respectively the second derivative FTIR and X-ray spectra of the composition of example 1.

Claims

1. Heterophasic compositions comprising starch, a thermoplastic polymer which is incompatible with starch and a plasticizer, in which the starch constitutes the dispersed phase and the thermoplastic polymer the continuous phase, said compositions having impact strength greater than 30 KJ/m² (measured on blown film having a thickness of 30 microns at 10°C and RH less than 5%).
2. Heterophasic compositions according to claim 1 comprising starch, a thermoplastic polymer which is incompatible with starch and a plasticizer, in which the starch constitutes the dispersed phase and the thermoplastic polymer the continuous phase, having impact strength greater than 30 KJ/m² (measured on blown film having a thickness of 30 microns at 10°C and RH less than 5%), and further characterised in that the X-ray diffraction spectrum of the compositions present a peak at an angle 2 theta in the range of 13 - 14° the ratio of the intensity of which in relation to that of the peak of the amorphous starch which appears at about an angle 2 theta of 20.5° is less than 2 and greater than 0.02.
3. Heterophasic compositions comprising starch, and a thermoplastic polymer which is incompatible with starch, in which the starch constitutes the dispersed phase and the thermoplastic polymer the continuous phase having impact strength greater than 30 KJ/m² (measured on blown film having a thickness of 30 microns at 10°C and RH less than 5%) obtainable by extrusion of a melt comprising starch, the thermoplastic incompatible polymer, a plasticizer liquid at room temperature used in amount from 2 to 8% on the weight of the starch and the thermoplastic polymer and water in amount less than 5% measured at the exit of the extruder before conditioning said melt being extruded by applying an extrusion energy of 0.2 to 0.5 Kw.h/Kg.
4. Compositions according to Claim 3, in which the quantity of plasticiser or mixture of plasticisers is between 3 and 7% by weight of the total of the starch and the thermoplastic polymer and the specific extrusion energy is from 0.2 to 0.5 Kw.h/Kg.
5. Compositions according to any of Claims 1 to 4 in which the starch-incompatible thermoplastic polymer is chosen from the group comprising the aliphatic polyesters obtainable from aliphatic hydroxyacids having 2 or more carbon atoms, or from the corresponding lactones or lactides, or from aliphatic dicarboxylic acids having 2 or more carbon atoms, and from diols having 2 or more carbon atoms, from aliphatic-aromatic copolyesters, polyester-amides, polyester-ether-amides, polyester-urethanes, polyester-urea and mixtures thereof.
6. Compositions according to Claim 5, in which the polyester is poly-epsilon-caprolactone, polyethylene or polybutylene-succinate, polyalkyleneadipate, diphenol diglycidylether polyadipate, polyalkyleneadipate-succinate, polyalkyleneadipate-epsilon-caprolactone, poly-epsilon-caprolactone/epsilon-caprolactame, polybutyleneadipate-co-terephthalate, polyalkylenesebacate, polyalkyleneazelate.
7. Compositions according to any of Claims from 2 to 6, in which the plasticiser is a polyhydric alcohol having from 2 to 22 carbon atoms.
8. Compositions according to Claim 7, in which the plasticiser is chosen from the group comprising glycerine, polyglycerol, glycerol ethoxylate, sorbitol acetate, sorbitol diacetate, sorbitol mono- and diethoxylate and mixtures thereof.
9. Compositions according to claim 8 wherein the plasticizer is glycerine.
10. Compositions according to any of Claims 1 to 9, including an interfacing agent chosen from the following classes of compounds:
 - a) esters of polyhydric alcohols with mono- or polycarboxylic acid with a dissociation constant pK less than 4.5 (compared to the pK of the first carboxylic group in the case of polycarboxylic acids), and a hydrophilic/lipophilic index (HLB) greater than 8;
 - b) esters of polyhydric alcohols with mono- or polycarboxylic acid having fewer than 12 carbon atoms, pK values of less than 4.5 and an HLB index of from 5.5 to 8;

- c) esters of polyhydric alcohols with C12-C22 fatty acids having an HLB index less than 5.5;
- d) non-ionic, water soluble surfactants; and
- e) reaction products of aliphatic or aromatic diisocyanates with polymers containing terminal groups reactive with the diisocyanate.

5

11. Compositions according to any of Claims from 1 to 10, presenting a band at 947cm⁻¹ in the second derivative FTIR spectrum thereof.

12. Manufactured products obtainable from the compositions of any of Claims from 1 to 11.

10

13. Films, sheets, bags, laminates, moulded articles, profiles, expanded sheets, thermoformed articles, expanded materials obtainable from the compositions of any of Claims from 1 to 12.

14. Shopping bags obtainable from the compositions of any of Claims from 1 to 11.

15

15. Mulch films obtainable from the compositions of any of Claims from 1 to 11.

16. Wrapping films obtainable from the compositions of any of claims from 1 to 11.

20

17. A method for preparing the compositions of any of Claims from 1 to 11, in which a melt comprising the starch, the starch-incompatible thermoplastic polymer, the plasticizer and water with a final content adjusted to less than 5% by weight, is extruded in an extruder provided with screws having a reverse profile for more than 30% of the length of the screw.

25

30

35

40

45

50

55

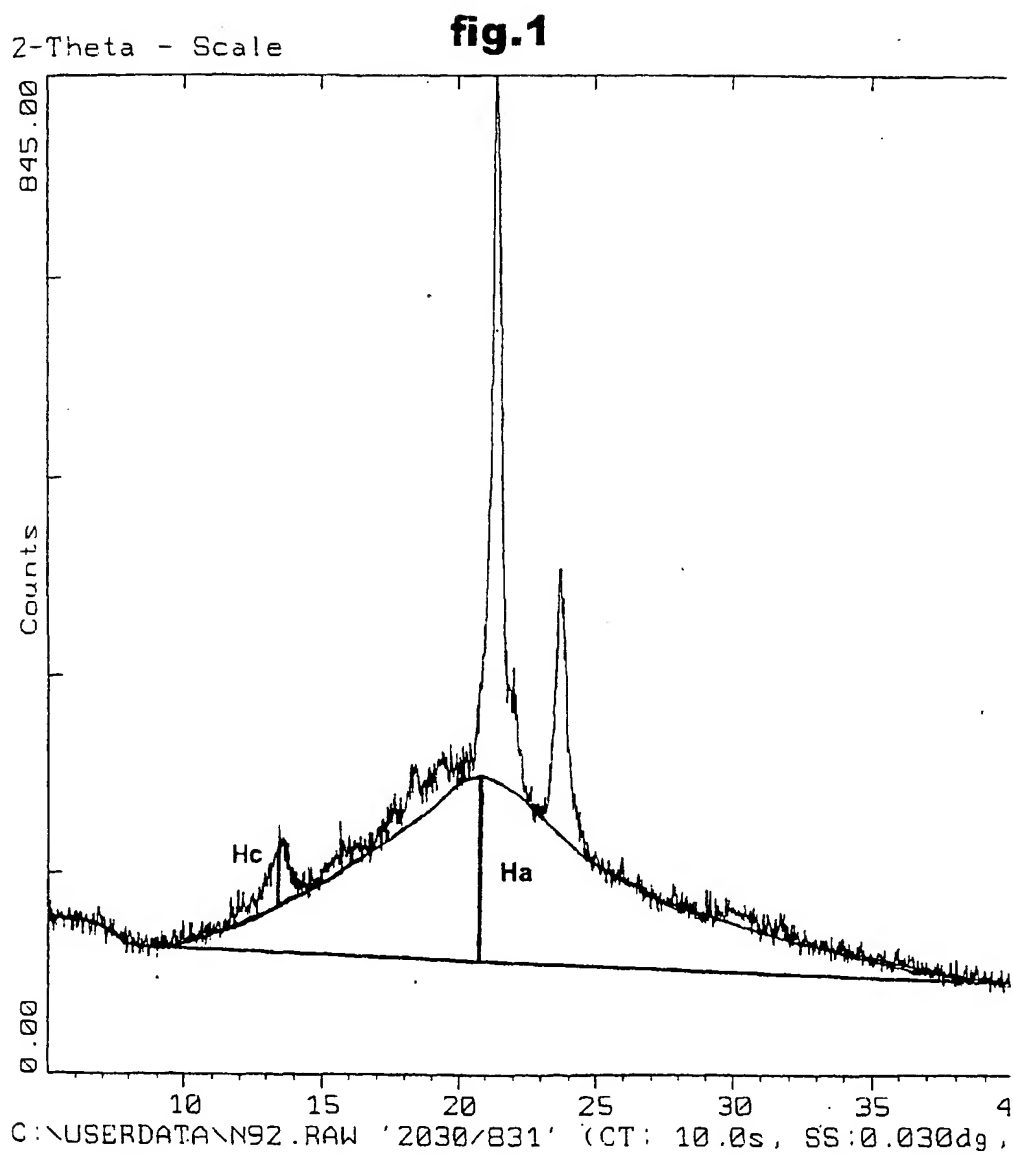
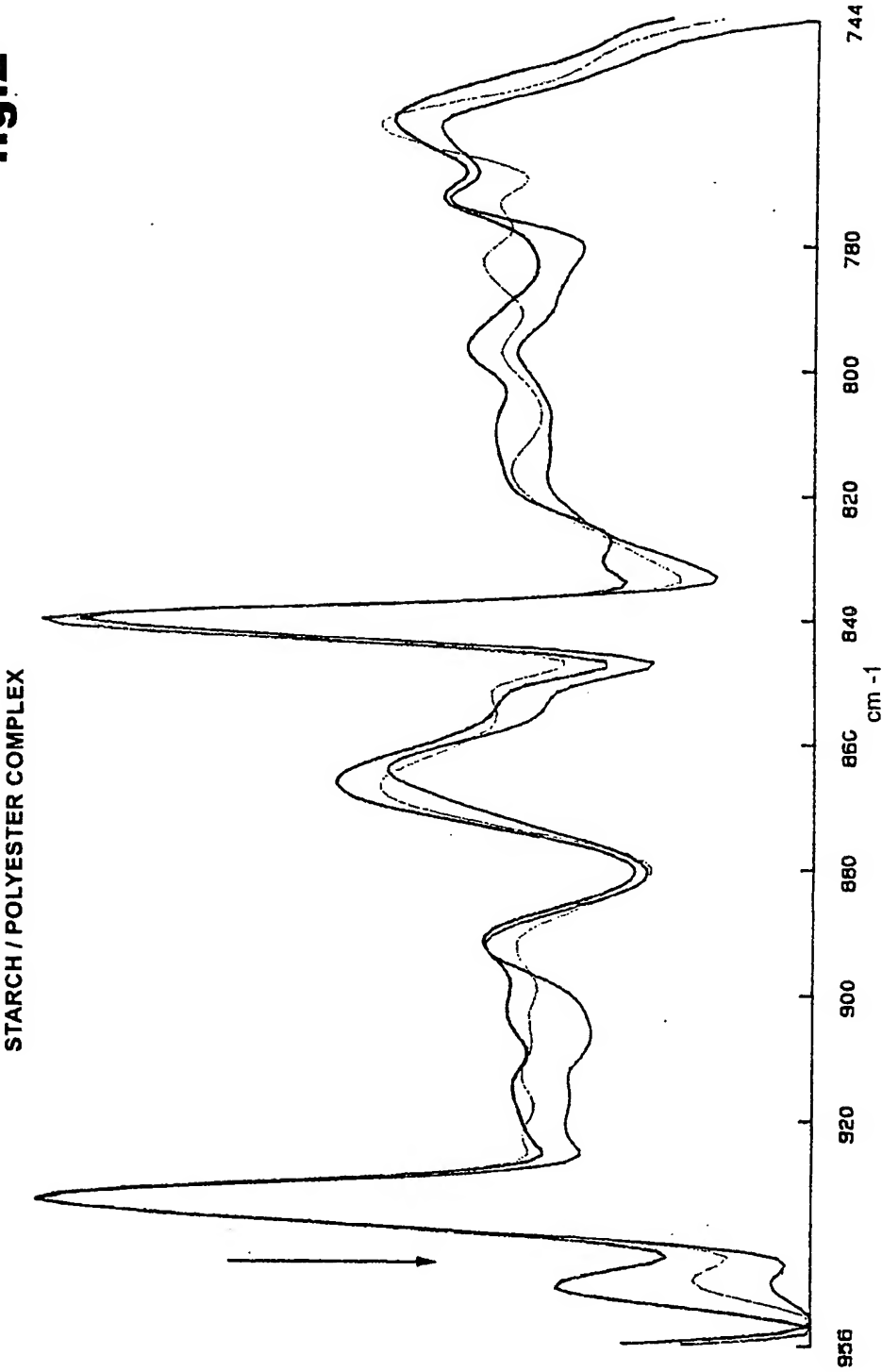


fig.2





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1955

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,Y	WO 98 20073 A (NOVAMONT) 14 May 1998 (1998-05-14) * page 14, paragraph 7 * * page 42 - page 44 * ---	1-17	C08L67/04 C08L3/02 C08J5/18 //(C08L67/04, 3:02)
Y	WO 95 24447 A (MICHIGAN STATE UNIVERSITY) 14 September 1995 (1995-09-14) * page 11, line 14 - line 18 * * page 16, line 5 - line 16 * * page 5, line 18 - line 22 * ---	1-17	
Y	US 5 362 778 A (FAMILI AMIR ET AL.) 8 November 1994 (1994-11-08) * column 4, line 30 - line 49 * ---	1-17	
A	EP 0 696 611 A (NOVAMONT) 14 February 1996 (1996-02-14) * page 3, line 11 - line 15 * ---		
D,A	US 5 412 005 A (CATIA BASTIOLI ET AL.) 2 May 1995 (1995-05-02) * example 2; tables 1-3 * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08L C08J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 September 1999	Examiner Lensen, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03 82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 1955

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-09-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9820073 A	14-05-1998	IT T0960890 A	05-05-1998
		IT T0960996 A	09-06-1998
		AU 5317498 A	29-05-1998
		EP 0937120 A	25-08-1999
		NO 992159 A	04-05-1999
WO 9524447 A	14-09-1995	US 5500465 A	19-03-1996
		CA 2183772 A	14-09-1995
		EP 0749460 A	27-12-1996
		JP 2813470 B	22-10-1998
		JP 9505107 T	20-05-1997
US 5362778 A	08-11-1994	CA 2115298 A	17-08-1994
		EP 0611804 A	24-08-1994
		JP 6248150 A	06-09-1994
EP 696611 A	14-02-1996	IT 1274603 B	18-07-1997
		AU 699169 B	26-11-1998
		AU 2844795 A	22-02-1996
		CA 2155594 A	09-02-1996
		CN 1123803 A	05-06-1996
		CZ 9502025 A	14-02-1996
		EP 0696612 A	14-02-1996
		FI 953761 A	09-02-1996
		HU 74032 A,B	28-10-1996
		JP 8059892 A	05-03-1996
		NO 953094 A	09-02-1996
		NZ 272733 A	24-02-1997
		PL 309923 A	19-02-1996
		SK 98295 A	04-12-1996
		US 5736586 A	07-04-1998
		ZA 9506602 A	19-03-1996
US 5412005 A	02-05-1995	EP 0525245 A	03-02-1993
		IT 1245485 B	20-09-1994
		IT 1256693 B	12-12-1995
		IT 1263114 B	30-07-1996
		CN 1077966 A,B	03-11-1993
		IL 104942 A	10-06-1997
		AT 155161 T	15-07-1997
		AU 658180 B	06-04-1995
		AU 1650992 A	21-12-1992
		AU 658207 B	06-04-1995
		AU 2058292 A	04-02-1993
		BR 9205258 A	27-07-1993
		CA 2074649 A	02-02-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 1955

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-09-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5412005 A		CA 2084994 A	04-11-1992
		CN 1071588 A	05-05-1993
		DE 9219021 U	27-02-1997
		DE 69220754 D	14-08-1997
		DE 69220754 T	04-12-1997
		DE 539541 T	30-01-1997
		DK 539541 T	15-09-1997
		WO 9219680 A	12-11-1992
		EP 0539541 A	05-05-1993
		ES 2103943 T	01-10-1997
		FI 925978 A	31-12-1992
		GR 3024078 T	31-10-1997
		JP 5228205 A	07-09-1993
		JP 2527523 B	28-08-1996
		JP 6502676 T	24-03-1994
		KR 9608112 B	20-06-1996
		LV 12151 A	20-10-1998
		LV 12151 B	20-12-1998
		RU 2095379 C	10-11-1997
		SK 390192 A	07-12-1994
		RU 2089151 C	10-09-1997
		US 5286770 A	15-02-1994
		AT 127034 T	15-09-1995
		DE 69204351 D	05-10-1995
		DE 69204351 T	11-04-1996
		DK 512360 T	18-09-1995
		EP 0512360 A	11-11-1992
		ES 2077280 T	16-11-1995
		GR 3017583 T	31-12-1995
		JP 5123550 A	21-05-1993
		PL 174799 B	30-09-1998
		US 5534150 A	09-07-1996
		AT 165385 T	15-05-1998
		DE 69318058 D	28-05-1998
		DE 69318058 T	10-09-1998
		EP 0560244 A	15-09-1993
		ES 2116364 T	16-07-1998
<hr/>			

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)